

III. "On the Physical Characters of the Lines in the Spark Spectra of the Elements." By W. N. HARTLEY, F.R.S., Professor of Chemistry, Royal College of Science, Dublin. Received March 18, 1891.

The properties of the atoms are a periodic function of their masses, and the physical characteristics of the spectra of the elements appear to be an expression of the properties of the atoms; for there is undoubtedly an intimate connexion between the rays emitted by the self-luminous vapours of the elements and their chemical and physical properties.

If we photograph the spark spectra of thirty or forty of the elements and arrange the spectra in groups following the periodic law, the arrangement will be seen to be a perfectly natural one. This observation applies not only to the groupings of the lines, but also to the physical characteristics of the individual lines. In spark spectra, the three most striking characteristics are (1) an extension of certain lines above and below that part of the spectrum bounded by the points of the two electrodes; (2) the nimbus which surrounds the extremities of the lines, even to some extent those portions which form an extension; and (3) the continuous spectrum which forms the background to the lines.

(1.) *On the Extension of the Lines.*—The spark discharge, as shown by Perrot, is composed of two parts, of which the fiery track, or central portion, is a statical discharge, and the aureole, or flame, is dynamical, and capable of electrolytic action.

From careful observation of the sparks, and photographs of spectra, I have come to regard all those spectra with lines extended as spectra of different discharges taken simultaneously. The principal lines lying between point and point of the electrodes are spectra of the fiery path of the spark; the extension of the principal lines above and below the points of the electrode appear to be spectra of the aureole. The principal observation which leads to this conclusion is that the electrodes are seen to glow silently and continuously above and below the points of the upper and lower electrodes, and frequently slight roughnesses present the appearance of brightly but steadily shining dots; particularly is this the case with those metals which exhibit the most extended lines, as for instance, cadmium, thallium, and indium. The lines in many spectra are free from this extension, and no glow is observed on the electrodes. A study of about thirty different spectra of the metals and semi-metallic substances has led to the following observation.

Elements which are difficult to volatilise, and those which are bad conductors of electricity, do not exhibit spectra with extended lines; and, con-

versely, metals which are the best conductors and the most volatile exhibit spectra with their principal lines largely extended.

The following metals are good conductors, that is to say, sufficiently good not to impede the spark when broad electrodes are used, and they are more or less volatile. They show a large extension of their principal lines :—

	Boiling point.	Atomic mass.		Volatility.	Atomic mass.
Magnesium..	1100° C.	24·4	Aluminium..	Not volatilised by ordinary means.	27·08
Zinc	924° to 954° C.	65·3	Indium	Volatilised at a red heat.	113·7
Cadmium ...	763° to 772° C.	112·1	Thallium....	Easily volatilised at a red heat.	204·2

		Atomic mass.
Copper	Not volatilised by ordinary means..	63·33
Silver.....	Boils about 1570° C.	107·93
Mercury.....	„ 357° C.	200·1

In these examples the extension of the lines is least in the case of the least volatile metals, which are also those of least atomic mass, and it is greatest with those which are most volatile and of greatest atomic mass.

The continuous spectrum in these examples is very weak, and the air lines are almost absent from the thallium and mercury spectra, the air spectra being suppressed by the excess of dense vapour in the track of the spark. The lines most extended are the following :—In the cadmium spectrum, those with wave-lengths $\overbrace{3611\cdot8, 3609\cdot6}$ (*a pair*), $\overbrace{3466\cdot8, 3465\cdot4}$ (*a pair*). These pairs appear as single lines if the dispersion is insufficient and the definition imperfect.

The most refrangible line of each pair is the more extended. The other lines in this spectrum are 3402·9, 2747·7, 2572·2, 2313·6, and 2265·9, all with fine extensions. In the spectrum of thallium, wave-lengths 3775·6, 3528·8, 3518·6, and 2917·7.

In the spectrum of mercury, the lines with wave-lengths 4358, 4046·5, and 3984 are well extended, but the most important extensions in this spectrum are the lines with wave-lengths 3662·9, 3654·4, 3632·9; the last of these, which form a well-marked triplet, is by far the most extended. The pair of lines 3130·4 and 3124·5 are greatly extended, and the same remark applies to 2966·4 and 2946·6.

The dimensions of the principal lines in the cadmium, thallium,

and mercury spectra were measured on my enlargements. The principal portion of the lines lying between point and point of the electrode was 42 mm. in all spectra. The extension of the lines *below* was 22 mm. to 25 mm., extension *above*, 9 mm. to 10 mm. As the extension is always sharp and well defined, it is an important feature in these spectra. Even concentrated solutions of the metals, when photographed with graphite electrodes, exhibit this extension in their principal lines. For instance a solution of beryllium chloride shows a very remarkable extension above and below the points of the upper and lower electrodes; the dimensions of the principal line, wavelength 3130·2, are as follows: between the points, 42 mm.; *below*, 10·5 mm.; *above*, 17·5 mm. It is at the upper or positive electrode that the longest extension is observed, but at the lower or negative electrode that it is strongest. In the case of the cadmium lines, the extension is smaller, but strong at the side of the negative electrode, and very fine and long at that of the positive.* The appearance of lines due to impurities or traces of metals in the spectrum of the negative electrode only, I have attributed to the oscillation of the spark discharge, and the fact that the negative electrode is the hotter.†

(2.) *The Nimbus*.—The nimbus is not apparently dependent on the volatility or the oxidisability of the vapour of the elements, though these properties are connected therewith.

By far the largest nimbus is that of magnesium; those of cadmium and mercury stand next in order; the smallest are those of platinum, gold, copper, and silver. It is thus evident that neither conductivity nor vapour density controls it, for there is very little nimbus on the lines of the thallium and iridium spectra; but volatility certainly increases it. There is a considerable nimbus on some of the lines in the spectra of arsenic, antimony, and bismuth; also on a few lines of tin and of lead. In the case of magnesium, the cause of the dense and large nimbus is probably the intensity of the chemical action of which the rays of the incandescent vapour are capable, together with the large quantity of metal in the track of the spark, owing to its volatility.

The chemical activity of the zinc rays is less than that of the rays of magnesium, but the effect of this is overbalanced by the density of the vapour and the volatility of the metal being both greater; accordingly the lines of zinc have a large nimbus. The nimbus is somewhat larger on the lines of cadmium than on those of zinc, the volatility and the density of the vapour are both greater.

* In a paper published in the 'Scientific Proceedings of the Royal Dublin Society,' on the constitution of electric sparks, this does not appear in the lithographed illustration, but I have carefully verified the fact by referring to the original photographs.

† *Loc. cit.*, p. 373.

The nimbus is evidently an expression of the quantity of matter in the spark, and the intensity of the chemical action which the rays emitted by its ignited vapour are capable of exerting.

(3.) *On the Continuous Spectrum which forms the Background to the Lines of certain Spectra.*—This must be caused by the ignition either of some solid substance or of a vapour which is not that of an element but an oxide. An examination of the spectra in which the continuous background of rays is a conspicuous feature discloses the fact that the metals which are not oxidisable do not possess it, for instance, gold, silver, and platinum. Metals of the iron group show it near the points of the electrodes when the non-volatile oxides are formed. The very volatile metals with volatile oxides, such as mercury, iridium, thallium, zinc, and cadmium, do not show it.

Spectra of the metalloids, such as tellurium, arsenic, antimony, and bismuth, which are not only volatile but which form volatile oxides, show it very strongly. Ordinarily, magnesium does not show it, because the exposure necessary for photographing the spectrum of that element is less by one-half the period of the others, and by one-quarter that of tellurium. When a plate is long exposed to the rays of magnesium, the continuous spectrum appears at the points of the electrodes where the non-volatile oxide would be formed. It may be considered that in the passage of the spark, the vapour of the element fills the track, and this vapour, on cooling, forms, for a minute period of time, an incandescent oxide, and, the spectrum of this being a continuous spectrum, its photograph appears as a background to the rays emitted by the element.

But it is nevertheless the fact that the continuous background is a very characteristic feature of the metalloids, though why the vapours of these oxides should produce this action more conspicuously than those of the oxides of the volatile metals, there seems to be no sufficient or well-understood reason to be advanced at present. It may be that the vapours of the metalloids in cooling emit a continuous spectrum for a short period prior to oxidation.

On the Breadth of Lines.—It is well known that, under identical conditions, the principal lines in the spectrum of an element become stronger and broader as the rays forming the spectrum proceed from a larger quantity of material, that is to say, form a denser radiating layer. It is evident, then, that in any series of three or more elements of similar character, the intensity and the breadth of the lines in their spectra will depend upon (1) intensity of chemical energy, (2) volatility and vapour density, and (3) electric conductivity of the metal.

In accordance with these conditions, the lines of cadmium are broader than those of zinc, and the lines of zinc broader than those of magnesium.